ASPECTS CONCERNING THE TREATMENT OF BIRCH VENEER WITH LIGNINS EPOXY DERIVATIVES WITH BIOCIDES PROPERTIES

ASPECTE PRIVIND TRATAREA FURNIRULUI DE MESTEACĂN CU DERIVAŢI DE LIGNINĂ EPOXIDAŢI CU PROPRITETĂŢI BIOCIDE

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Abstract. *The paper presents the results regarding the interactions between birch venner and some biocides based on lignin epoxy derivatives and copper ions. Lignin derivatives have been synthesized using annual plant lignins (wheat straw and Sarkanda grass) and commercial products (Protobind 1000, 2000, 3000) offered by the Granit Recherche Developement SA company, Lausanne-Schwitzerland. The treatments with unmodified and epoxy lignins were applied to birch veneer strips by immersing them in copper chloride solutions. The lignin products were dissolved in fufuryl alcohol of 5% concentration. The biostability of treated veneer have been tested by burying into soil for six months. The samples were than characterized by the loss of weight and the contact angle values. The results obtained show that the treatment of veneer with complex of lignin epoxy derivatives and copper solutions offer a high stability of the woody substrate compared with the unmodified products*

Key words: lignin, epoxydation, veneer, biocides, biostability, contact angle.

Rezumat. *Lucrarea prezintă rezultatele privind interacţiunea dintre furnirul de mesteacăn şi o serie de biocizi pe bază de derivaţi de lignină epoxidaţi şi ioni de cupru. Derivaţii ligninici au fost sintetizaţi folosind ca substrat lignine din plante anuale (paie de grâu şi Sarkanda grass) şi produse comerciale (Protobind 1000, 2000, 3000) oferite de firma Granit Recherché Dévelopement S.A. Lausanne-Schwitzerland. Tratamentele cu lignine nemodificate şi epoxidate, au fost aplicate furnirului de mesteacan şi s-au bazat pe imersarea acestuia în soluţii de clorură de cupru. Produsele ligninice utilizate au fost dizolvate în alcool furfurilic în concentraţie de 5%. Biostabilitatea probelor de furnir astfel tratate a fost testata prin îngroparea lor în sol timp de şase luni şi caracterizate prin pierderile de masă şi valorile unghiului de contact. Rezultatele obţinute evidenţiază că tratamentul aplicat furnirului folosind complecşi ai derivaţilor epoxidaţi de lignină cu ionii de cupru, oferă o stabilitate ridicată a substratului lemnos studiat comparativ cu produsele nemodificate.*

Cuvinte cheie: lignină, epoxidare, furnir, biocizi, biostabilitate, unghi de contact.

INTRODUCTION

Nowadays, the methods used for the protection of wood and wood product are based on the utilization of several substances toxic for microorganism and insects, but usually all these products present a huge inconvenience being incompatible with the environment. The natural wood suffers biodegradation processes under the action of biological agents determined by environmental factors and conditions of storage or use after processing. Thus, depending on their structure, the chemical constituents of wood will be degraded in order: hemicelluloses, cellulose and lignin. Studies performed in this field have shown that preservative agents penetrate only less ordered areas of cellulose and hemicelluloses polymers. In the case when copper is used in ammonia systems, ammonia is wholly or partially evaporated and as the result, copper is precipitated. A part of copper ions are fixed in the substrate timber through carboxyl or hydroxyl groups or wood which are present in ionized state at high pH conditions.

The present study is taking in consideration the remarkable properties of the lignin polymer, especially its resistance to biological attack, and also the toxic potential of copper ions. The main purpose is to investigate the biostability of birch wood and how it is influenced by the systems created from renewable products: unmodified lignin or chemically modified lignin (Th. Măluţan et al., 2007, 2008, A.M. Căpraru et al., 2008, 2009, V.I Popa, 1983), in the absence or presence of copper ions. The functionality of lignin is involved especially by its complexation capacity of copper ions, which explains the formation of synergistic process, which contributes to an increase of the biostability. That is why the outher sphere of copper (II) ions used in the treatment (chloride or tetra amino copper hydroxide) seems play a role in the surface protection process (E. Ungureanu et al., 2008).

MATERIAL AND METHOD

In this investigation the following materials have been used: birch veneer samples with 1x10 cm dimensions, Wheat Straw lignin (L1), Grass lignin (L2) and three commercial products as: Protobind 1000, Protobind 2000 and Protobind 3000 (Pb) (also the same products modified by epoxidation reaction (LE) and (PbE) provided by Granite Company (Switzerland) and copper chloride ($CuCl_2$), tetra amino copper hydroxide (Cuam) and furfuryl alcohol (AF).

The same dimensions birch veneer samples have been used in the investigation. All aforementioned substances have been dissolved in furfuryl alchohol (5% concentration). The following treatments were applied:

1. Immersion of the samples during five minutes in different solutions prepared preliminarily, followed by drying in laboratory conditions (25^0C).

2. Immersion of the samples in copper containing solutions and drying of the samples followed by tratament with lignin and lignin derivatives and another drying. The samples with one of these trataments applied were weighed to determine the quantity of material retained on the surface of birch veneer samples. After that, the samples were buried in soil and were maintained in laboratory conditions for a period of six months with regular watering in order to maintain specific soil moisture. The

degree of biodegradation was evaluated by determining the mass loss and contact angle variations for the treated samples, using goniometer Krüss Model FM40 Easy Drop. The experimental data it is processing with *Mathcad Professional 2001* program (Diaconescu R., 2001).

RESULTS AND DISCUSSIONS

Firstly, the mass loss was determined for each birch veneer samples after six months of burial in soil. The results of mass loss for different veneer samples treated with various biocides containing unmodified lignin or epoxy lignin and copper ions are presented in figures 1-3. It can be observed that in the case of the samples containing lignin or lignin derivatives and copper ions the degradation process is inhibited, and the degree of biostability is higher for the complex combinations, of treatments components.

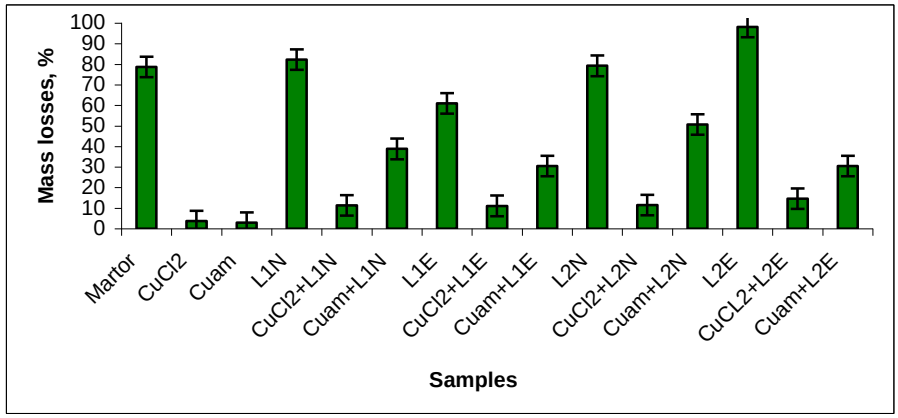

Fig. 1. Variation of mass losses for the veneer samples non-treated and treated

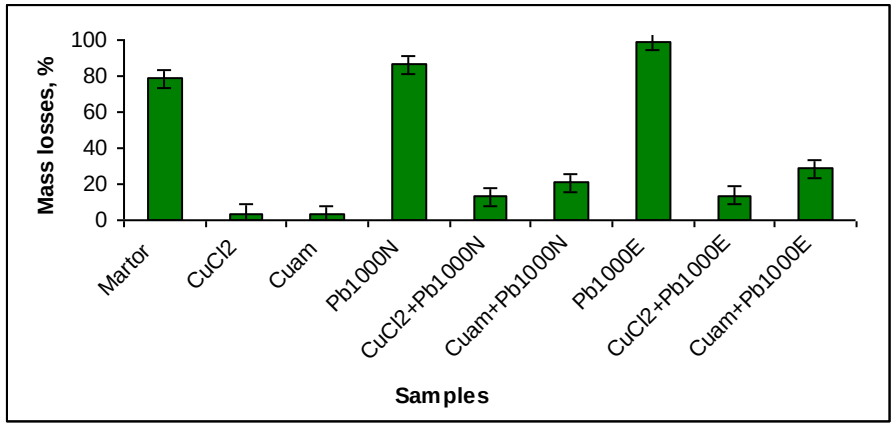

Fig. 2. Variation of mass losses for the veneer samples non-treated and treated

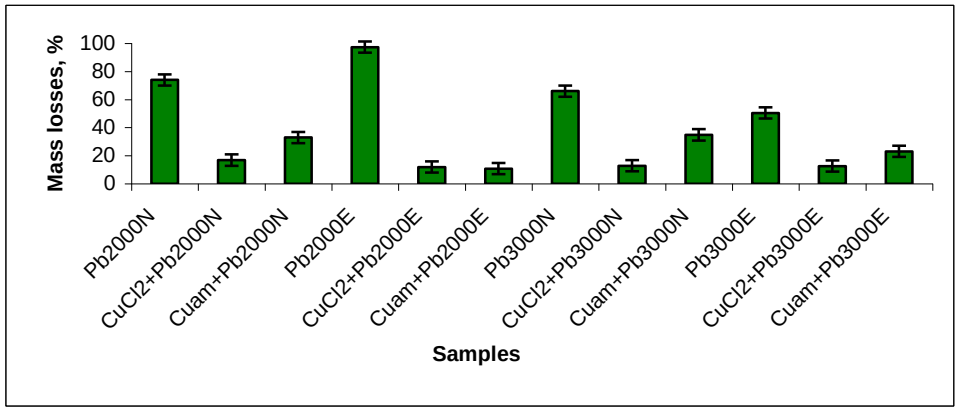

Fig. 3. Variation of mass losses for the veneer samples non-treated and treated

The presented results have lead to the idea that the effectiveness of the surface treatment of wood product depends on the type of the treatment components and the degree of functionality of the samles. The analysis of the mass loss variations seem to indicate that the slightest mass loss occurred in specimens treated with copper ions and complexes epoxydated lignins. At the same time, the birch veneer samples treated only with copper ($CuCl_2$ or Cuam) present a high inhibition degree of biodegradation. Copper-based compounds are substances that produce an effective bioprotection on timber. The obtained results indicate that efficiency is the highest for the samples treated with the following biocides: $CuCl_2$ > Cuam, > $CuCl_2$L1E > $CuCl_2$Pb1000N > CuamPb2000E > $CuCl_2$Pb3000E, presenting mass losses in the range of 3-12 %.

Most significant mass loss occurred in the case of the veneer samples treated with epoxy lignin and unmodified lignin, the mass losses reaching almost 99 % (the case of Pb1000 E lignin). This situation may be determined by the low level of the interaction between the veneer and the product used for the treatment and higher accessibility of several components from the tested samples to the action of soil microorganisms, which can find favorable conditions for the development and deep attack on the wood substrate. To enquire the effectiveness of the applied treatments on the veneer surface, another parameter was determined - the contact angle. The decrease of the contact angle is good evidence for the substrate hydrophilic and for the increase of the wetting capacity. The variation of the contact angle for samples of birch plywood treated with various biocides systems based on copper ions, modified and unmodified lignin and their complexes is presented in figures 4 and 5.

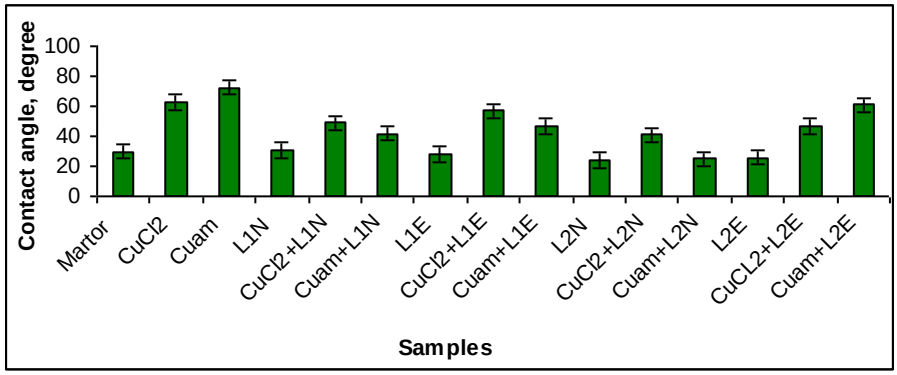

Fig. 4. Variation of contact angle for the veneer samples non-treated and treated

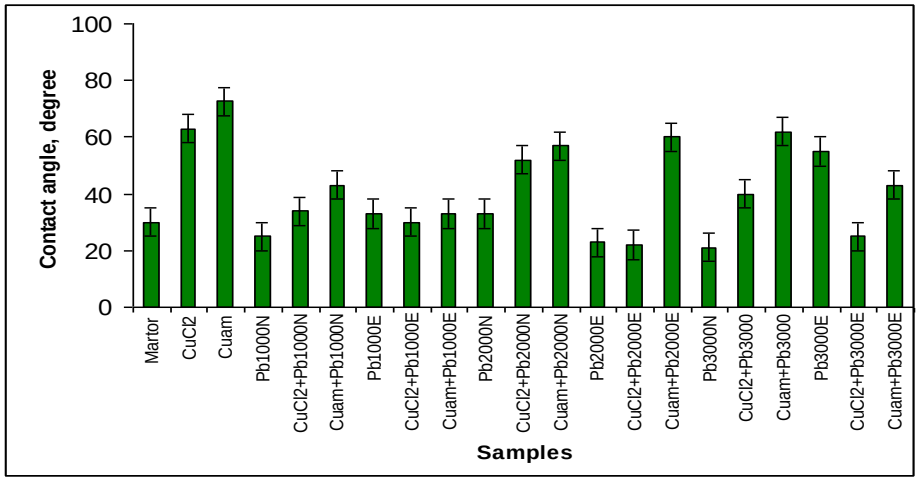

Fig. 5. Variation of contact angle for the veneer samples non-treated and treated

As it can be observed from figures 4 and 5, the treatments performed using only unmodified and epoxidated lignins in the treatment of wood surface produce a penetration capacity even higher than of distilled water in solid media. On the contrary, the treatments with copper (II) solutions especially tetra amino copper hydroxide (Cuam) also their complexes with various epoxidized lignins, determined a low degree of the wetting, the contact angle being high, ensuring a high biostability. The highest values for the contact angle are observed in the case of the samples treated with the following biocides: Cuam > CuamL2E, > CuamPb1000N > CuamPb2000E > CuamPb3000N > CuamPb3000E > $CuCl_2$ and are consistent with the lowest values of mass losses.

The surfaces of these materials are very difficult to analyze because of a highly advanced level of the degradation in some samples and the contact angle values decrease sharply during the measurement, this being caused by a very hydrophilic surface. Although the contact angle value is higher in the case of the samples mentioned above, the water penetrates rather rapidly the wood substrate,

and only if the samples treated only with copper ions, the contact angle showed a slighter decline during the determination. It can be concluded that the chemical modification of lignin ensures a higher biostabilisation of the wood surface in comparison with the cases where unmodified lignins are used as the components of the treatment.

CONCLUSIONS

1. The modification of lignin by epoxidation provides higher biostability of wood substrate than unmodified products; the mass losses being munch lower in this case.

2. The treatments with different solutions of copper ions ensure a higher degree of protection, as expected, the biostability being even higher than in the case of lignin products.

3. The complexation of lignin and their derivatives (epoxidated lignins) with copper (II) ions increases stability of the veneer samples, but it is still lower in comparison with that offered by the simple copper ions.

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